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PRODUCTION OF PIGMENTS WITH A PEROVSKITE-LIKE STRUCTURE BASED ON NICKEL TITANATE BY THE PRECIPITATION METHOD

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The possibility of producing ceramic pigments based on the NiO – TiO₂ system by hydroxide coprecipitation from aqueous salt solutions is investigated. The synthesized pigments have good chromophore parameters and are stable up to a temperature of 1200°C. Practical recommendations are made.

The purpose of the present study is to investigate the possibility of producing ceramic pigments with a perovskite-like structure based on the NiO – TiO₂ system by precipitation from aqueous salt solutions. Synthesis and investigation of pigments were implemented similarly to the studies described in [1, 2].

Nickel typically has the degree of oxidation 2+ and coordination numbers 4 and 6; therefore, its complexes have the tetrahedral and octahedral spatial configurations. Tinting produced by nickel varies depending on the type of the complex. Under the effect of ligands the complexes are deformed and their structure becomes distorted, which modifies the position of the absorption bands.

Tinting of nickel (II) compounds in aqueous solutions can vary from violet-blue to green, yellow-green, and brown [3]. In contrast to aqueous solutions, the color of ceramic pigments containing Ni²⁺ depends as well on the structure of the crystal lattice that serves as the basis for pigment synthesis. Thus, if in the synthesis of garnet-type pigments, for instance, grossularite 3CaO · Al₂O₃ · 2SiO₂, one introduces Ni²⁺ instead of Ca²⁺, the pigments have a green color [4], which is typical of Ni²⁺ with coordination number 6. If the coordination number of Ni²⁺ is equal to 4, the pigments have a light blue color.

To obtain stable tinting, the charges and ionic radii of nickel and the element to be replaced have to be close. In the same way as Ni²⁺ ions are able to replace Ca²⁺ ions in grossularite, they can replace them in perovskite as well. In this case the perovskite crystalline lattice will be distorted, since the ionic radii (by Goldschmidt) of Ni²⁺ (0.78 Å), Ca²⁺ (1.06 Å), and Ti⁴⁺ (0.64 Å) are different. Consequently, pigments of a perovskite-like structure will be produced. The color of such pigments will depend not only on Ni²⁺ but also on the Ti⁴⁺ ion, which is located in the center of a cube and is

surrounded by six oxygen atoms [5]. Three forms are typical of TiO₂: rutile, anatase, and brookite. They are all constructed of octahedral atom groups but the octahedra are linked in different ways.

In order to expand the palette of ceramic pigments of the perovskite-like structure, they were synthesized by coprecipitating difficultly soluble compounds from solutions, and after heat treatment pigments were obtained. The following compounds were the initial reactants: NiSO₄, Ti(SO₄)₂, and TiO₂. Precipitation was carried out using 1 M solution of NaOH and NH₃ solution (1 : 1) from aqueous solutions of salts with a concentration of 0.5 M. To synthesize some samples, crystalline TiO₂ was introduced into the NiSO₄ solution, after which heterogeneous precipitation was implemented. The precipitator was introduced into the system before reaching a pH value corresponding to complete precipitation of ions, which was identified from the equivalence point on the pH -titration curves (a ÉV-74 universal pH meter).

Precipitation of Ni(II) hydroxide ends with pH = 10.6 (Fig. 1, curve 1). The hydroxide of Ti(IV) starts precipitating in a highly acid medium at pH ~ 1. In this case the equivalence point at pH = 6.9 (curve 2) indicates the end of neutralization of sulfuric acid, which is introduced into the initial salt solution to suppress hydrolysis. Titration curve 3 of the solution Ni(II) – Ti(IV) differs from the titration curves of individual salts. It exhibits one jump with an equivalence point at pH = 5.6. In the absence of chemical reactions between Ni(II) and Ti(IV) two clearly expressed jumps correlating with consecutive precipitation of hydroxides ought to be registered on the titration curve, due to a substantial difference in the solubility of Ni(OH)₂ (solubility limit $SL = 2.0 \times 10^{-15}$) and Ti(OH)₄ ($SL = 6.3 \times 10^{-52}$) [6].

Consequently, Ni(II) and Ti(IV) in alkali precipitation react with each other; however, the curve shape is not typical

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of the formation of a mixed hydroxide. Presumably, a compound of the nickel titanate type NiTiO_3 is formed. In the case of heterogeneous precipitation, titration curve 4 is similar to titration curve 1, which does not indicate any reactions between the components during precipitation.

The resulting precipitates were investigated by the IR spectroscopy method (Specord-75IR) before and after thermal treatment (Table 1 and Fig. 2). All spectra of air-dried samples have absorption bands related to the valence vibrations of molecular water and hydroxyl groups ($2800 - 3700 \text{ cm}^{-1}$), deformation vibrations of H_2O molecules ($1617 - 1632 \text{ cm}^{-1}$), and valence vibrations of the $\text{Me} - \text{O}$ bond ($400 - 700 \text{ cm}^{-1}$) [7]. The high intensity of these bands points to a substantial content of nonstructural water in precipitates dried at room temperature.

The deformation vibrations of the OH^- group in the spectrum of $\text{NiO} \cdot n\text{H}_2\text{O}$ are manifested in the form of a doublet band of medium intensity ($1035 - 1085 \text{ cm}^{-1}$) and in the spectrum $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ in the form of a band at 1032 cm^{-1} [7]. This band is not registered in the precipitate spectrum, which points to the probable formation of NiTiO_3 salt instead of hydroxide and agrees well with pH titration data. Furthermore, this precipitate has a simpler spectrum than that of $\text{NiO} \cdot n\text{H}_2\text{O}$: the intense narrow band of the valence vibrations of water at 3637 cm^{-1} is missing, and the number of absorption bands typical of $\text{NiO} \cdot n\text{H}_2\text{O}$ in the range of $400 - 1700 \text{ cm}^{-1}$ is significantly smaller. The spectrum is not additive with respect to the spectra of individual hydroxides. Consequently, a new chemical compound not containing OH^- groups has been formed in alkali precipitation, namely, nickel titanate NiTiO_3 .

After calcination of the precipitate with ratio $\text{Ni} : \text{Ti} = 1 : 1$ at 1200°C (Table 1) all absorption bands in its spectrum are in the range of $427 - 1186 \text{ cm}^{-1}$, the highest intensity exhibited by the bands reflecting the range of vibrations of the $\text{Me} - \text{O}$ bond ($400 - 700 \text{ cm}^{-1}$). On the one hand, this spectrum has a simpler form than the spectrum of the same precipitate before calcination due to the absence of absorption bands of water molecules and OH^- groups. On the other hand, this spectrum has more absorption bands within the range of vibrations of the $\text{Me} - \text{O}$ bond than the spectrum of the same sample before calcination, which shows that the sample changes from an amorphous state to the crystalline one. Furthermore, the intensity of these bands is higher than in the non-calcined precipitate.

In the spectrum of calcined precipitate one can distinguish high-intensity bands at 464 and 536 cm^{-1} and medium-intensity bands at 896 and 1086 cm^{-1} . The spectrum of the same precipitate before calcination (Fig. 2, curve 3) exhibits three low-intensity bands at 552 , 640 , and 847 cm^{-1} . The total difference between the bands observed in these spectra shows that the types of bonds in the precipitate undergo significant changes in calcination.

The spectrum of $\text{NiO} \cdot n\text{H}_2\text{O}$ has high-intensity bands at 443 , 460 , and 532 cm^{-1} , medium intensity at 600 , 1110 , and

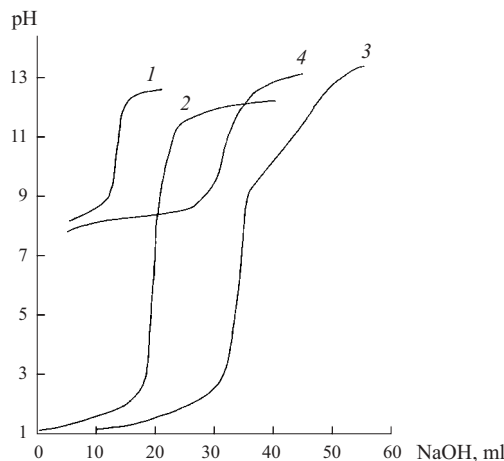


Fig. 1. Curves of pH titration of alkali solution: 1) NiSO_4 ; 2) $\text{Ti}(\text{SO}_4)_2$; 3) $\text{NiSO}_4 + \text{Ti}(\text{SO}_4)_2$; 4) $\text{NiSO}_4 + \text{TiO}_2$.

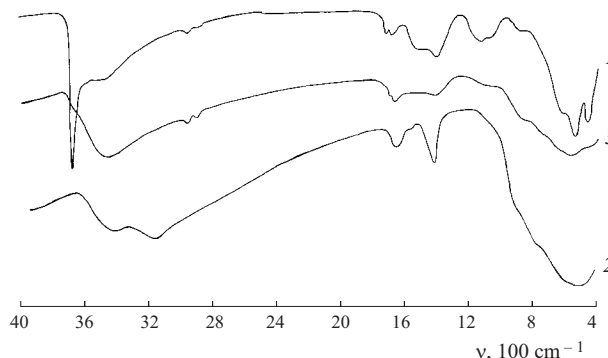


Fig. 2. IR spectra of air-dried samples: 1) $\text{NiO} \cdot n\text{H}_2\text{O}$; 2) $\text{TiO}_2 \cdot n\text{H}_2\text{O}$; 3) precipitate obtained from $\text{Ni}(\text{II}) - \text{Ti}(\text{IV})$ solutions with molar ratio $\text{Ni} : \text{Ti} = 1 : 1$.

1147 cm^{-1} , and low intensity at 1035 and 1085 cm^{-1} . Comparing the frequencies of the spectra of $\text{NiO} \cdot n\text{H}_2\text{O}$ and the calcined precipitate, the three absorption bands in the latter spectrum can be attributed to the vibrations of the $\text{Ni} - \text{O}$ bonds (464 , 536 , and 1086 cm^{-1}). A correlation of the band

TABLE 1

Sample	Composition	Temperature, $^\circ\text{C}$	Absorption maximums, cm^{-1}
1	NiO	1000	840, 850, 980, 1620
2	$\text{NiO} \cdot \text{TiO}_2$ (heterogeneous precipitation)	1000	480, 1085
3	$\text{NiO} \cdot \text{TiO}_2$ (heterogeneous precipitation)	1200	464, 536, 896, 1085
4	$\text{NiO} \cdot \text{TiO}_2$ (precipitation from salt solution)	1200	480, 1090, 1140, 1170
5	TiO_2 (rutile) [8]	—	420, 520, 610, 660, 1600

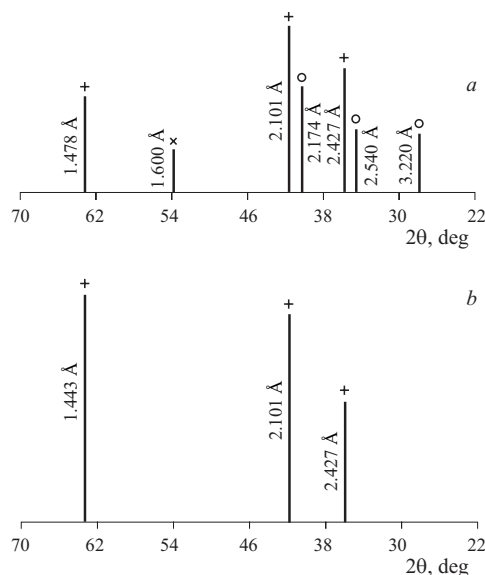


Fig. 3. Diffraction patterns of samples $\text{NiO} \cdot \text{TiO}_2$ produced by the powder technology (a) and in thermal treatment of coprecipitated hydroxides (b): +) NiTiO_3 ; x) NiO ; o) TiO_2 .

at 896 cm^{-1} , which was not observed in the spectrum of $\text{NiO} \cdot n\text{H}_2\text{O}$, remained unclear.

Evidence of chemical bonds between Ni(II) and Ti(IV) can be the modification of the vibration band intensities of the $\text{Ni} - \text{O}$ bond at $460 - 464$ and $532 - 536 \text{ cm}^{-1}$ with respect to each other: the intensity of the second one in the $\text{NiO} \cdot n\text{H}_2\text{O}$ spectrum is higher than that of the first one, and in the calcined precipitate spectrum it is the reverse. Moreover, the spectrum of this precipitate does not contain an intense band of the $\text{Ni} - \text{O}$ bond vibration at 443 cm^{-1} , which is observed in the spectrum of $\text{NiO} \cdot n\text{H}_2\text{O}$. Since the position of the absorption bands correlated with the $\text{Ni} - \text{O}$ bond in the precipitate significantly changes, this means that the new bond $\text{Ni} - \text{O} - \text{Ti}$ has become prevalent.

The position of the absorption bands in the IR spectra of calcined samples is represented in Table 1. Absorption maxima of rutile are absent in the spectra of all samples of $\text{NiO} \cdot \text{TiO}_2$ [8]. The spectrum of NiO produced from $\text{NiO} \cdot n\text{H}_2\text{O}$ by calcination at a temperature of 1000°C (sample 1) has a set of intense bands in the range $800 - 1700 \text{ cm}^{-1}$, i.e., after heat treatment the long-wave absorption bands are shifted to a higher-frequency range compared to the initial sample. Sample 2 obtained after calcination at 1000°C of nickel hydroxide precipitated in the presence of solid TiO_2 has a very simple IR spectrum consisting of two bands at 480 and 1085 cm^{-1} . Since the spectrum of NiO (sample 1) does not contain these bands and the number of bands in this spectrum is smaller than in each individual oxide, one can assume the formation of a new compound: nickel titanate.

An increase in the temperature of heat treatment of sample 3 up to 1200°C produces a modification in the spectrum:

high-intensity bands arise at 464 and 536 cm^{-1} , which are attributed to vibrations of the $\text{Ni} - \text{O}$ bond, and a medium-intensity band at 896 cm^{-1} . The absorption band at 1085 cm^{-1} does not undergo changes. Consequently, with temperature growing from 1000 to 1200°C , the type of $\text{Me} - \text{O}$ bonds in the sample significantly changes, since all modifications in the spectra are registered in the range of vibration of the specified bonds. This corroborates the stability of NiTiO_3 up to the specified temperature.

Sample 4 synthesized at the same temperature from coprecipitated hydroxides has no absorption bands at 536 and 896 cm^{-1} , but its spectrum has blurred wide bands at 1140 and 1170 cm^{-1} that are not separated from the band of 1090 cm^{-1} , presumably due to residual amorphousness of the sample.

The results of IR spectroscopic studies indicate that coprecipitation of hydroxides of two metals or precipitation of nickel hydroxide in the presence of TiO_2 produces a new chemical compound, which under subsequent thermal treatment passes from an amorphous state into a crystalline state and represents nickel titanate.

Samples obtained after heat treatment of synthesized precipitates for 1 h at a temperature of 1200°C were studied by x-ray phase analysis (DRON-2 with URS-504, ionization registration of scattered rays). Deciphering was carried out using the ASTM x-ray pattern database. For comparison purposes similar samples were synthesized using the traditional powder technology. The data obtained (Fig. 3) show that at 1200°C the reaction of the formation of NiTiO_3 from chemically precipitated mixtures is more intense: the x-ray diffraction pattern exhibits reflections belonging only to NiTiO_3 with a perovskite structure. In the case of synthesis of nickel titanate from oxides, the pattern besides exhibits the reflections of both phases that served as sources for the high-temperature synthesis.

Thus, the formation of NiTiO_3 with the perovskite structure is corroborated, and it is established that stabilized nickel titanate with a stable crystalline lattice is formed from chemically precipitated mixtures at lower temperatures than from powders. The color of the pigments obtained on the basis of this compound is yellow. The pigments in an amount of $3 - 5\%$ can be used to tint glaze coatings of ceramic tiles.

The proposed technology of hydroxide coprecipitation of salts of nickel (II) and titanium (IV) or heterogeneous precipitation of nickel hydroxide (II) in the presence of solid TiO_2 with subsequent washing, drying, firing, and milling has certain advantages over the current powder technology of pigment production, since such energy-consuming processes as milling initial components and drying suspensions are eliminated. The purity of the synthesized pigments is higher due to eliminating milling impurities, and thermal treatment temperature is lower. The proposed method can be recommended for producing pigments with good chromophore characteristics.

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